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Field and Laboratory Methods for Investigating a Marine Gasoline Spill

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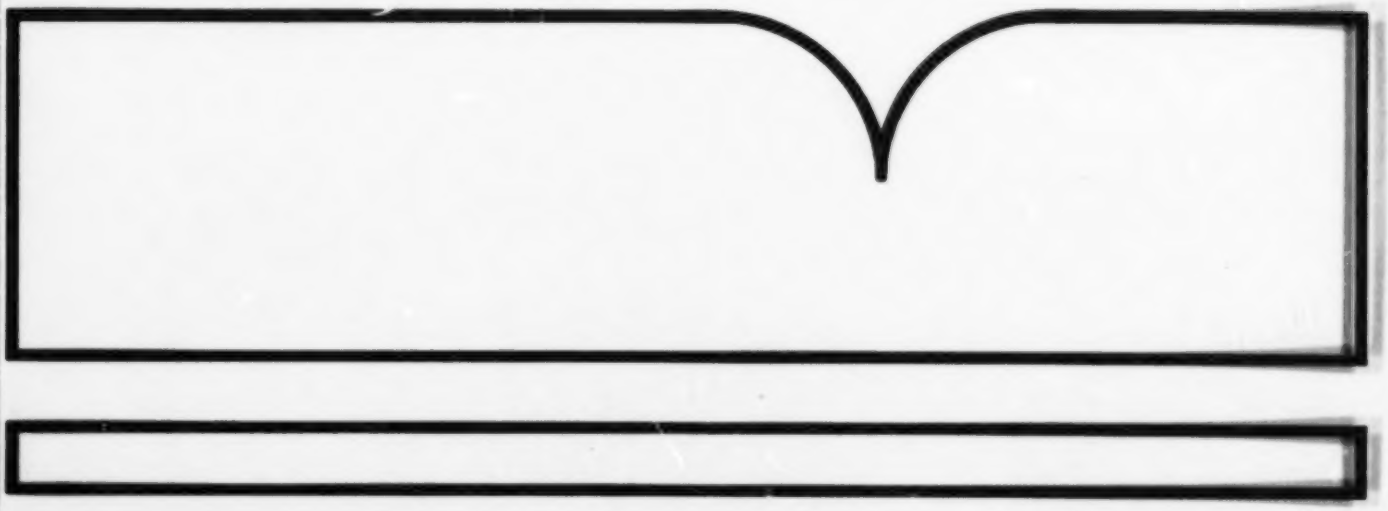

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16. ABSTRACT

Samples of water and bivalve mollusks were collected during the 2-day period immediately following a spill of gasoline in Block Island Sound, RI, and were analyzed by gas chromatography and gas chromatography-mass spectrometry. These analyses showed gasoline compounds in the water column at concentrations up to 20 µg/L even though a visible slick was not present. Additionally, very low levels of hydrocarbons, which might have originated from the gasoline spill, were detected in bivalves from the area. The analytical protocol used for examining these water samples was carefully evaluated for its expediency and accuracy in detecting gasoline compounds in a field sampling situation. The method proved to be rapid, introduced only minimal levels of contamination, and consistently returned 60 % of the gasoline compounds. Although it is difficult to quantitatively handle volatile organic compounds in a field sampling situation, this study indicated that a marine gasoline spill could be quickly and effeciently monitored by using the described methods.

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Field and Laboratory Methods for Investigating a Marine Gasoline Spill

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■ Samples of water and bivalve mollusks were collected during the 2-day period immediately following a spill of gasoline in Block Island Sound, RI, and were analyzed by gas chromatography and gas chromatography–mass spectrometry. These analyses showed gasoline compounds in the water column at concentrations up to 20 μg/L even though a visible slick was not present. Additionally, very low levels of hydrocarbons, which might have originated from the gasoline spill, were detected in bivalves from the area. The analytical protocol used for examining these water samples was carefully evaluated for its expediency and accuracy in detecting gasoline compounds in a field sampling situation. The method proved to be rapid, introduced only minimal levels of contamination, and consistently returned 60% of the gasoline compounds. Although it is difficult to quantitatively handle volatile organic compounds in a field sampling situation, this study indicated that a marine gasoline spill could be quickly and efficiently monitored by using the described methods.

Introduction

On March 16, 1978, the *Ocean Barge 250* grounded on Watch Hill Reef (41° 17.40′ N, 71° 51.50′ W) ~1000 m off Watch Hill, RI (Figure 1). It subsequently released 1900 metric tons of gasoline into the waters of Block Island Sound before it was pulled free by the U.S. Coast Guard, almost 24 h later. The resulting slick was driven away from coast by northeast winds, and it apparently dispersed and evaporated during the following 48 h.

While the ecological effects of spills of crude oil (*1–3*), No. 2 fuel oil (*4, 5*), and bunker C and No. 6 fuel oil (*6, 7*) have been extensively investigated, only limited data are available concerning the environmental effects of gasoline spills. Accordingly, two cruises were conducted aboard the R/V Strider on March 17 and 18 to sample the water column and the benthos in an attempt to investigate the impact of this unique event (*8*).

The problems associated with the collection, transport, and storage of small- and large-volume water samples containing hydrocarbon pollutants have been thoroughly addressed (*9*). Contamination of the samples by fuel oils and grease from the oceanographic vessel, adsorption of sample hydrocarbons by the walls of sampling and storage bottles, and biodegradation and photolysis of hydrocarbons require particular attention (*10*). To overcome these difficulties we have adapted a method for examining rather volatile hydrocarbon pollutants in water samples which utilizes on-board liquid–liquid extraction followed by transfer of extracts to the laboratory and analysis by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

This accident presented an opportunity to evaluate this method in its application to sampling and measuring gasoline compounds in seawater samples that were collected during the response to a spill situation. The study presents the results of this evaluation.

Methods

Water Column. Water samples were obtained on the first cruise (March 17, 1 day after the spill) at the stations denoted with a triangle in Figure 1, in the order no. 1, 3, 4, 7, 2, and 11. These six liter samples were taken with a Niskin bottle at a depth of 3.5 ± 0.5 m. In an attempt to minimize the problems characteristic of transport and storage of such samples (i.e., contamination, adsorption by container walls, loss due to volitization, and degradation of organic sample components (*10*), they were transferred directly from the Niskin bottles to glass separatory funnels and each one was immediately extracted with 300 mL of methylene chloride. These resulting extracts were then stored in glass bottles with Teflon-lined caps. Water extractions were facilitated by the use of a specially designed heavy-duty funnel shaker, and, following each extraction, funnels were rinsed with methylene chloride before sampling the next station. This procedure required less than 30 min per station.

Later, at the EPA laboratory, these extracts were passed through Na_2SO_4 to remove residual water and particulate material and then reduced in volume in a Kuderna–Danish evaporator fitted with a three-ball Synder reflux column. The samples were solvent exchanged to hexane, reduced in volume under a stream of nitrogen to 0.1 mL, and stored at −5 °C. The samples were never evaporated to dryness to prevent an excessive loss of the more volatile low-molecular-weight components of the gasoline. Procedural blanks were processed along with samples in order to determine whether contamination had occurred.

These extracts were then analyzed by gas chromatography, and the resulting chromatograms were quantified by inte-

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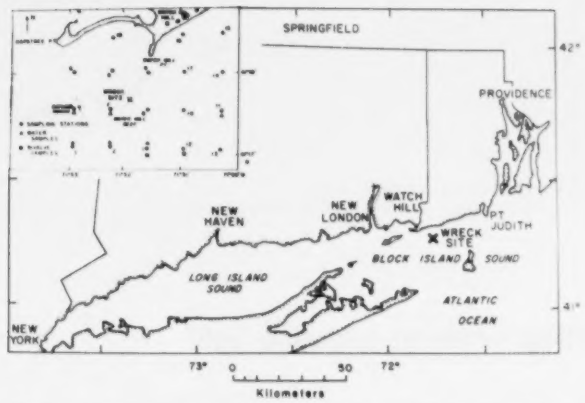

Figure 1. Map showing the location of the *Ocean Barge 250* gasoline spill at Watch Hill, RI, and the station locations sampled during the cruises on March 17 and 18.

grating the areas of peaks ranging from peak 1 (C_2-benzene) through peak 15 (C_2-naphthalene) and comparing these areas with those obtained from direct analysis of known alkylbenzene and alkylnaphthalene standards.

To establish the capability of the analytical protocol to recover the various gasoline components, we utilized a cryogenic GC analysis (−65 to +250 °C at 5 °C/min) of a neat gasoline standard (1 part no. 1 port tank; 1 part no. 2 port tank). (Gasolines were obtained from the barge by the U.S. Coast Guard at Groton, CT.) This was followed by a conventional analysis (35 °C for 4 min, then 5 °C/min to 250 °C) of a gasoline standard in hexane (prepared by diluting the same neat standard with hexane to 1000 ng/μL). Comparison of the two analyses showed which of the lower-molecular-weight components were obscured by the characteristic GC solvent front. A water-accommodated fraction of the neat gasoline was also prepared (conventional analysis) (20 mL neat gasoline shaken with 2 L of seawater, allowing the mixture to separate for 6 h, and then extracting the water with the described method). Comparison of this analysis with that of the neat gasoline revealed any changes caused by sample handling and analysis.

A correction factor for procedural losses was established by determining the quantitative recovery of gasoline spiked into seawater and extracted by using the described methods.

Benthos. Samples of bivalve mollusks were obtained on the second cruise (March 18) at the stations denoted with a square in Figure 1. Samples of *Modiolus modiolus* and *Mercenaria mercenaria* were collected at station 1 with a rocking chair dredge, and samples of *Acquipecten irradians* were collected at station 12 with a trawl. Samples were packed in ice and then frozen at the EPA laboratory until analyzed. Thawed samples were dissected, and the tissues then digested for 16 h at 37 °C in 4 N NaOH in glass centrifuge bottles. The digested tissues were then extracted with methylene chloride. The organic phase was passed through a column of Na_2SO_4 and silica gel to remove water and interfering material and subsequently reduced in volume and solvent exchanged to hexane. All fractions were reduced in volume to 0.1 mL under a stream of nitrogen and stored at −5 °C. As with the water samples, these extracts were never evaporated to dryness. Procedural blanks were also processed to determine whether contamination had occurred. The extracts were then analyzed by GC and/or GC–MS, and the results were compared with those from the analyses of gasoline standards.

Water and bivalve samples were analyzed by using a Hewlett Packard 5840-A gas chromatograph equipped with SE-54, SE-52, and OV-101 glass capillary columns and a splitless injection port. The gas-chromatographic–mass-spectrometric

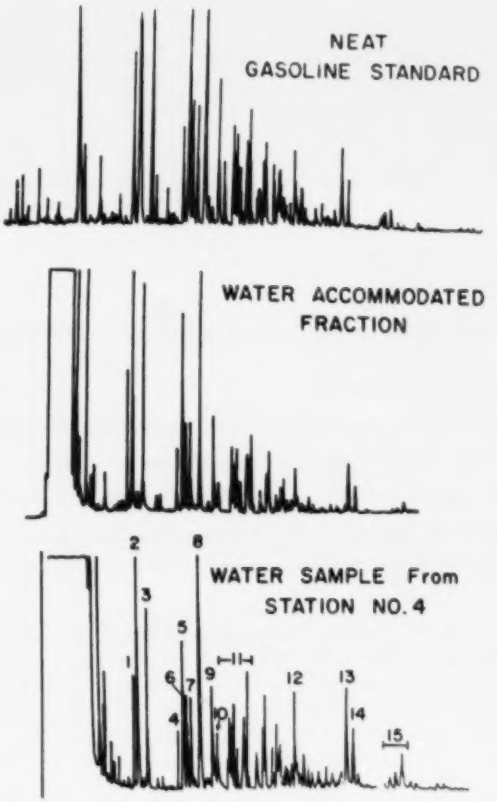

Figure 2. A comparison of gas chromatograms of a neat gasoline standard (−65 °C; 250 °C; 5 °C/min: 20-m SE-54 column), a water-accommodated fraction (WAF) of the gasoline standard (35 °C for 4 min, then 5 °C/min to 250 °C: 30-m SE-52 column), and a water sample from station 4 (35 °C for 4 min, then 5 °C/min to 250 °C: 30-m OV-101 column).

analyses were performed on a 30-m OV-101 glass capillary column in a Schimazdu Model GC-4CM GC interfaced with a Finnegan 1015 mass spectrometer equipped with a Systems Industries Data System and Riber 400 D8 software.

Results

Gas chromatograms of extracts from the water samples from stations 3, 4, and 7 revealed a pattern of peaks that was qualitatively similar to the pattern from the water-accommodated gasoline standard (Figure 2). Comparisons of gas chromatograms of water samples from these stations with those from the water-accommodated gasoline and neat gasoline standards revealed a relative loss of lower-molecular-weight compounds in the water samples (Figure 2). GC–MS analyses of the water sample from station 4 showed that the compounds present included *m/e* 106 (C_2-benzenes, peaks 1–3), 118 (indane, peak 10), 120 (C_3-benzenes, peaks 4–9), 128 (naphthalene, peak 12), 134 (C_4-benzene, peak 11), 142 (2-methylnaphthalene and 1-methylnaphthalene, peaks 13 and 14), and 156 (C_2-naphthalene, peak 15). These compounds are characteristic of gasoline (*11*).

A comparison of the analysis of the neat gasoline standard (−65 °C; +250 °C; 5 °C/min) with that of the standard diluted in hexane (35–250 °C at 5 °C/min) revealed that only 5–10% of the peaks were obscured by the solvent front on chromatograms. Further comparison of the neat standard with the analysis of the water-accommodated fraction suggested rather minimal changes in the pattern of gasoline compounds due to procedural handling (Figure 2). However, there was a relative loss of the lowest-molecular-weight compounds. While

these results indicated that almost all of the gasoline compounds in the water samples could be detected by the method used, the procedural efficiency showed that a portion of each of these individual compounds was lost during sample handling and analysis. The return for gasoline compounds spiked into seawater was quite consistent and ranged from 50% (C_2-benzenes) to 70% (C_2-naphthalenes). Average recovery for all compounds was ~60%.

Table I lists the stations in the sequence that they were sampled. Whereas samples from stations 3, 4, and 7 showed 5, 17, and 20 μg of gasoline compounds/L, the samples from stations 1 and 11 showed no detectable gasoline, and the sample from station 2 showed only trace levels. These reported values show that the levels of gasoline at adjacent sites varied considerably (e.g., stations 7 and 2) and that no gasoline components were detected at the first and last station sampled. These observations suggest that contamination of the sampling bottle by gasoline from the water samples did not occur.

Gas chromatograms of extracts from most of the shellfish tissues showed some resemblance to those obtained from gasoline standards, but interfering peaks were also prominent. GC–MS analysis of the extract of *Mercenaria mercenaria* identified some of the peaks as alkylbenzene and alkylnaphthalene compounds, although they were at very low levels (<1 ng/g (wet weight)).

Chromatograms of procedural blanks for both the water and tissue methods showed only very small peaks, and these did not significantly interfere with the analysis of samples.

Discussion

The results of this study showed that the analytical methodology described could be successfully applied to a spill situation where no observable gasoline slick was present. Sampling with a Niskin bottle followed by on-board liquid–liquid extraction and then volume reduction in the laboratory with GC and GC–MS analyses constituted a rapid, clean, and relatively efficient method for collecting and analyzing gasoline compounds in seawater samples. If a slick had been present, contamination of the sampling bottle would likely have occurred (*10*) and thereby biased the analyses.

Control samples and procedural blanks showed that only low levels of contamination had occurred. Additionally, a comparison of the analysis of the neat gasoline standard with that of the standard diluted in hexane showed that GC analysis obscured measurement of only 5–10% of the earliest eluting compounds with the solvent front. Analysis of the water-accommodated fraction of the standard showed minimal alterations in the pattern of gasoline compounds as a result of procedural handling. The analytical window for this procedure was therefore clean and included 95% of all the gasoline compounds present.

Results of the experiment that determined the procedure's extraction efficiency for recovering gasoline compounds from the water-accommodated fraction indicated that the method consistently returned 50% of the lower-molecular-weight compounds (C_2-benzenes) and 70% of the higher-molecular-weight compounds (C_2-naphthalenes). Quantification of these components at several points during the volume-reduction phase of analysis showed that, as the sample extract size decreased, the more volatile compounds were lost at a greater rate than the less volatile ones. Water samples obtained at the spill showed an even more dramatic relative loss of low-end components. This additional loss probably reflects volatilization of gasoline to the atmosphere before sampling at the spill site.

Northeast winds, 3–4-ft seas, and the high volatility of gasoline were apparently responsible for the rapid dissipation of this slick. A U.S. Coast Guard survey flight over the spill area on March 17 (1 day after the spill) detected no signs of a slick, and, although gasoline vapors were very strong at the Watch Hill Coast Guard Station the afternoon of the spill, there was no evidence of gasoline on the water or in the air during any of the R/V Strider cruises.

Table I. Concentrations of Gasoline-Range Hydrocarbons in Water Samples Taken Off Watch Hill Reef

sample	C_8–C_{12} hydrocarbon concn (C_2-benzenes–C_2-naphthalenes)[a]
station 1	background value
station 3	5 μg/L
station 4	17 μg/L
station 7	20 μg/L
station 2	trace levels
station 11	background value

[a] Concentrations tabulated here have been corrected for procedural losses and assume a recovery of 60%.

Nevertheless, an examination of the water samples clearly indicated that gasoline had in fact become incorporated into the water column. Stations 3, 4, and 7, southwest of Watch Hill Reef in the area where the slick moved before dissipating, showed the presence of gasoline compounds (Table I; Figure 1). GC–MS analyses of extracts from these water samples indicated that alkylated benzenes, indane, naphthalene, and alkylated naphthalenes were present. Samples from station 1, to the south of Watch Hill Reef, and from control station 11, to be east, did not show detectable levels of gasoline compounds.

Gas chromatograms of extracts from the shellfish suggested the presence of low levels of gasoline compounds, but their correlation with chromatograms from gasoline standards was insufficient to serve as conclusive evidence of contamination by the spill. GC–MS analysis identified some of the compounds present in *Mercenaria mercenaria* as alkylated benzenes and alkylated naphthalenes. These analyses were not considered to confirm that gasoline from the spill had been incorporated by the organisms examined, however, because adequate control samples from the spill site that could be used to establish the background level of such contaminants were not available. The unavailability of adequate control samples is one of the more common problems associated with damage assessment from petroleum spills (*12*). Alternate possible sources for these compounds include other petroleum fuels and municipal and industrial wastes.

Some investigations on the accumulation and depuration of hydrocarbons from petroleum by filter-feeding bivalves have shown that hydrocarbons accumulated as an acute dose (such as that from a spill) were rapidly depurated (*13, 14*). These studies suggest that, if the alkylbenzenes and alkylnaphthalenes found in these bivalves resulted from the *Ocean Barge 250* gasoline spill, they would probably have been rapidly depurated.

The toxicity of gasoline and its individual components to marine organisms has been established through several laboratory research efforts (*15–18*), and the U.S. EPA has listed the lethal toxicity of kerosene (which has a large number of aromatic hydrocarbons in common with gasoline) for larval forms at 0.1 mg/L (*19*). The concentrations found here 1 day after the spill (20 μg/L) were lower than these, but much higher levels were probably present in the water column immediately following the spill. Organisms in the vicinity therefore may have been affected.

Very little information is available concerning the environmental impact of gasoline spills, but Bugbee and Walter (*20*) did report a 2.5-yr biological survey of a freshwater creek

where 5000 gal of aviation gasoline was spilled in 1969. They found the impact to be severe, with almost a threefold reduction in species diversity and nearly a full year required for complete recovery of the ecosystem.

Marine field assessment studies often involve tremendous logistical problems. Handling and storage of equipment and samples is a major consideration in the design of any spill response effort, and, therefore, rapid and simple methods such as those used here are of particular interest. The analyses in this study suggest that the measurements were reliable and that gasoline spilled from the barge did in fact penetrate the water column in the vicinity of Watch Hill Reef. Alkylated benzenes and alkylated naphthalenes were found in water samples at depths of up to 3.5 m. Because of the difficulties in extrapolating laboratory toxicity tests to field situations, and because of the paucity of information concerning the impact of gasoline spills in the environment, it is difficult to estimate the damage inflicted by the *Ocean Barge 250* spill. Nevertheless, the potential long-term, low-level synergistic effects on marine organisms should not be ignored.

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